

METHOD AND APPARATUS FOR TREATING AMMONIA-CONTAINING GAS

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Technical Field

The present invention relates to a method and an apparatus for treating
5 an ammonia (NH_3)-containing gas, and particularly to a method and an
apparatus for defusing NH_3 in an exhaust gas or NH_3 expelled from waste
water to a vapor phase; namely, the method and apparatus for treating an NH_3 -
containing gas which can oxidize and decompose highly efficiently NH_3 of a
high concentration into nitrogen.

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Background Art

Large quantities of an exhaust gas and waste water containing NH_3 are
discharged from a variety of industrial plants such as semiconductor factories,
resulting in a variety of bad effects such as odor environmental pollution, and
15 deterioration of water quality. Particularly, in recent years, eutrophication of
sea water such as generation of red tides due to NH_3 contained in industrial
waste water becomes a social problem; and in this respect, laws for severely
restricting NH_3 concentration in waste water are going to be developed. For
this reason, a variety of studies and developments are made on a technology
20 for defusing NH_3 ; and the following technologies are going to become
mainstreams as a treating technology for exhaust materials containing NH_3 .

Namely, a method for catalytically oxidizing NH_3 with a catalyst is known
as a technology for decomposing NH_3 in a vapor phase, while a method for
catalytically oxidizing NH_3 by using the above-mentioned catalyst after
25 transferring NH_3 in waste water to a vapor phase in an aeration tower or a
stripping tower is known as a technology for decomposing NH_3 contained in
industrial waste water. These technologies are ones drawing attention as a
method for using a multifunctional catalyst having a denitration function due to
a denitration active component and a function of oxidizing NH_3 to form a

nitrogen oxide (NO_x) due to a noble metal component in combination in the catalyst, whereby, several % of NH₃ may be converted efficiently into harmless nitrogen (N₂), for example.

Patent document 1: Japanese Patent Application Laid-Open No. 5-146634

5 Patent document 2: Japanese Patent Application Laid-Open No. 2000-317272

Disclosure of the Invention

Problems to be Solved by the Invention

However, the above-described prior art involves such problems that a
10 catalyst itself is deteriorated thermally due to oxidative reaction heat of NH₃,
and that a reaction to generate nitrogen monoxide (NO) from NH₃ proceeds
excessively due to temperature rise in a catalyst layer in the case where an
NH₃ concentration in an exhaust gas or an NH₃ concentration transferred to a
gas is high. More specifically, there have been such problems that when an
15 NH₃ gas of a high concentration contained in an exhaust gas is made to be
harmless by means of a tube reactor filled with a multifunction catalyst
(hereinafter referred to as "NH₃ decomposition catalyst"), oxidation heat of NH₃
concentrates in an inlet part of the catalyst to reduce a life of the catalyst, and
that a denitration function becomes unbalanced with respect to a function of
20 generating NO from NH₃, whereby large quantities of by-products such as NO_x
are produced due to temperature rise by reaction heat.

In order to avoid such problems, a method in which a publicly known
high heat-resistant noble metal-base oxidation catalyst layer 12 is disposed on
the upstream side of an NH₃ decomposition catalyst layer 2 as shown in FIG. 5
25 to convert in advance a part of NH₃ into NO_x, and then the resultant gas is
introduced into the above-described NH₃ decomposition catalyst layer 2 has
been proposed. In the method, however, there arises such a problem that an
NH₃ oxidation reaction due to the above-described noble metal-base oxidation

catalyst layer 12 is thermally run away by means of reaction heat to by-produce a large quantity of NO_x in the case where an NH₃ concentration is high in the exhaust gas. Furthermore, the method involves also such fear that a ratio of NH₃ to be decomposed in advance varies excessively when a gas flow rate and
5 an NH₃ concentration change, so that the NH₃ cannot perfectly be decomposed in the downstream part.

An object of the present invention is to eliminate the problems involved in the above-described prior art and to provide a method and an apparatus for treating an NH₃-containing gas by which NH₃ contained in a high concentration
10 in an exhaust gas can be efficiently decomposed and treated to be converted into a harmless gas without causing the deterioration of a catalyst and the increase in production of by-products.

Means for Solving the Problems

15 The above-described problems can be solved by such a method that a gas containing NH₃ of a high concentration is allowed to pass through a pre-treatment catalyst layer composed of a catalyst layer having a function of oxidizing in advance NH₃ to generate NO_x and another catalyst layer not having such function as described above disposed in parallel thereto, and then
20 the resultant gas is allowed to be in contact with an NH₃ decomposition catalyst layer having a denitration function, i.e. a function for catalytically reducing a nitrogen oxide and a function for oxidizing NH₃ to generate NO_x in combination.

Namely, the inventions of this application are as follows.

(1) A method for treating an NH₃-containing gas, characterized by
25 passing the ammonia (NH₃)-containing gas through a pre-treatment catalyst layer provided with a catalyst layer having a function for oxidizing NH₃ to generate nitrogen monoxide (NO) and another catalyst layer not having the former function in parallel, and then passing the resultant gas through a

catalyst layer having a denitration function in combination with a function for oxidizing NH_3 to generate NO.

(2) The method according to the paragraph (1), wherein that a part of a flow path section is provided with a catalyst layer containing an NH_3 oxidation active component selected from zeolite, silica, titania, zirconia and alumina supported with platinum (Pt), palladium (Pd), or Rhodium (Rh); and another part of the flow path section is provided with a catalyst layer not containing the NH_3 oxidation active component, to form the pre-treatment catalyst layer.

(3) The method according to the paragraph (1) or (2), wherein the catalyst having the denitration function in combination with the function for oxidizing NH_3 to generate NO contains titanium oxide (TiO_2); an oxide of at least one of vanadium (V), tungsten (W) and molybdenum (Mo); and zeolite, titania, alumina, or zirconia supported with platinum (Pt).

(4) The method according to any one of the paragraphs (1) to (3), wherein a feed amount of the NH_3 -containing gas to a flow path of the catalyst layer having the function for oxidizing NH_3 to generate NO in the pre-treatment catalyst and a flow path of the catalyst layer not having the former function is controlled such that an NH_3 concentration in the gas treated in the pre-treatment catalyst layer is higher than a NO_x concentration.

(5) The method according to any one of the paragraphs (1) to (4), wherein the NH_3 -containing gas is the gas after transferring the NH_3 in waste water to a vapor phase.

(6) An apparatus for treating an NH_3 -containing gas in which a pre-treatment catalyst layer having a function for oxidizing NH_3 to generate carbon monoxide (NO), and a catalyst layer having a denitration function in combination with another function for oxidizing NH_3 to generate NO are sequentially disposed in a flow path section of a gas containing ammonia (NH_3) along the gas flow direction, characterized in that a part of the flow path section

is composed of a catalyst layer containing an NH_3 oxidation active component selected from zeolite, silica, titania, zirconia, alumina and the like supported with platinum (Pt), palladium (Pd), or Rhodium (Rh); and another part of the flow path section is composed of a catalyst layer not containing the NH_3 oxidation active component in the pre-treatment catalyst layer.

(7) The apparatus according to the paragraph (6), wherein a ratio of the catalyst layer containing the NH_3 oxidation active component to the catalyst layer not containing the oxidation component in the pre-treatment catalyst layer is decided such that the NH_3 concentration in the outlet gas of the pre-treatment catalyst layer is higher than a NO_x concentration in the outlet gas.

(8) A pre-treatment catalyst used in the apparatus according to the paragraph (6) or (7), wherein a part of the flow path section is composed of a catalyst layer containing an NH_3 oxidation active component selected from zeolite, silica, titania, zirconia and alumina supported with platinum (Pt), palladium (Pd), or Rhodium (Rh); and another part of the flow path section is composed of a catalyst layer not containing the NH_3 oxidation active component.

Effect of the Invention

According to a first aspect of the present application, an NH_3 concentration in the gas flowing into the NH_3 decomposition catalyst layer on the downstream side can be reduced to a concentration suitable for an NH_3 decomposition reaction in the NH_3 decomposition catalyst layer by means of the pre-treatment catalyst layer on the upstream side. Thus, even a gas containing NH_3 of a high concentration can be efficiently treated without accompanying thermal deterioration of the catalyst layer and without increasing production of NO_x as a by-product.

According to a second aspect of this application, in addition to the above-described advantageous effect of the invention, an NH_3 concentration in an exhaust gas can be reduced to a concentration in which the exhaust gas can be treated in the NH_3 decomposition catalyst layer on the downstream side by means of the pre-treatment catalyst, a part of the flow path of which is composed of the catalyst layer containing an oxidation active component supported with a noble metal.

According to a third aspect of this application, in addition to the above-described advantageous effects of the invention, the NH_3 in the NH_3 -containing gas with the concentration thereof reduced to a predetermined concentration may be efficiently decomposed and treated by balancing the denitration function with the function for oxidizing NH_3 to generate NO by using the NH_3 decomposition catalyst layer containing a predetermined metal and a noble metal.

According to a fourth aspect of this application, in addition to the above-described advantageous effects of the invention, the NH_3 concentration in the outlet gas of the pre-treatment catalyst layer may be increased efficiently to be higher than the NO_x concentration.

According to a fifth aspect this application, even waste water containing an NH_3 of a high concentration can be efficiently decomposed to be made harmless after transferring the NH_3 in the waste water to a vapor phase, in addition to the above-described advantageous effects of the invention.

According to a sixth aspect of this application, an NH_3 concentration in the gas flowing into the NH_3 decomposition catalyst layer on the downstream side can be reduced to a concentration suitable for a treatment in the NH_3 decomposition catalyst layer, and hence, an NH_3 -containing gas of a high concentration can be efficiently treated without employing diluent air, water

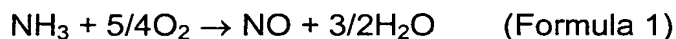
vapor or the like, or with employing a quantity consumed thereof reduced to the utmost.

According to seventh and eight aspects of this application, a part of the NH₃ contained in an exhaust gas can be oxidized efficiently to NO.

5 Based on FIG. 3, the principle of the present invention will be described.

FIG. 3 is a graphical representation showing examples of temperature dependency of NH₃ oxidation ratio due to a noble metal supported catalyst such as Pt, Pd, and Rh in the case where an NH₃ concentration is high (thick line) and the case where the NH₃ concentration is low (thin line).

10 An NH₃ oxidation reaction in the presence of a noble metal supported catalyst is represented by the following formula 1; and the reaction accompanies remarkable exothermic heat.



Thus, when an NH₃ concentration is high, a temperature of the
15 processed gas rises due to oxidation reaction, whereby the reaction speed becomes faster, so that changes in the NH₃ oxidation ratio exhibit a rapid rising characteristic shown by the thick line in FIG. 3. Since there is such a rapid rising characteristic, the NH₃ oxidation ratio changes to a value close to either 0% or 100% due to a slight change in the inlet temperature, the NH₃
20 concentration or a gas amount. Accordingly, as in the prior art mentioned above, even if such treatment that a noble metal-base oxidation catalyst layer is disposed on the upstream side of the NH₃ decomposition catalyst layer to oxidize partially the NH₃ in a previous stage, whereby the NH₃ concentration is reduced, and then the resultant gas is introduced into the NH₃ decomposition
25 catalyst layer is intended to apply, most of the NH₃ is oxidized to NO_x by means of the noble metal-base oxidation catalyst layer in the upstream part. Hence, there arises such a problem that the NO_x is discharged in an untreated condition to the outside of the system.

On the other hand, according to the present invention, a catalyst layer having a function for oxidizing NH_3 to generate NO , i.e. a catalyst layer supported with a noble metal catalyst and a catalyst layer supported with no noble metal catalyst have structures in which a catalyst layer 3 containing NH_3 oxidation component and another catalyst layer 4 not containing the oxidation component exist mixedly as shown in each sectional structure of, for example, FIGS. 2(A), 2(B), and 2(C) in a pre-treatment catalyst layer. Under the circumstances, even when substantially 100% oxidation of NH_3 arises in the catalyst layer 3 supported with a noble metal catalyst, the NH_3 passing through the catalyst layer 4 supported with no noble metal catalyst remains in an undecomposed condition. Accordingly, when each ratio of gas amounts passing through the catalyst layer supported with the noble metal component and the catalyst layer supported with no noble metal component (a ratio of catalyst flow paths occupying the respective sections) is selected, NH_3 of a high concentration can be oxidized partially in a desirable ratio. As described above, when a gas to be treated has been previously passed through the pre-treatment catalyst to reduce an NH_3 concentration in the gas flowing into the NH_3 decomposition catalyst layer on the downstream side, NH_3 in the gas can be efficiently decomposed without causing the NH_3 decomposition catalyst to have an abnormal high temperature. In this case, it is preferred to adjust the condition such that an NH_3 concentration is higher than a NO_x concentration. Thus both the concentrations of the NH_3 and the NO_x can be reduced down to several ppm or less by means of synergistic actions of denitration reaction and NH_3 oxidation reaction inside the catalyst. These reactions are represented by the following formulae 2 and 3.

Denitration reaction: $\text{NH}_3 + \text{NO} + 1/4\text{O}_2 \rightarrow \text{N}_2 + 3/2\text{H}_2\text{O} \dots$ (Formula 2)

NH_3 oxidation reaction inside catalyst: $\text{NH}_3 + 5/4\text{O}_2 \rightarrow \text{NO} + 3/2\text{H}_2\text{O} \dots$
(Formula 3)

Brief Description of the Drawings

FIG. 1 is a diagram showing a basic configuration of an NH_3 -containing gas purifier applied to the present invention.

FIGS. 2(A), (B), and (C) are views each showing a structural example of a pre-treatment catalyst layer applied to the present invention.

FIG. 3 is a complementary representation for explaining the principle of the present invention.

FIG. 4 is an explanatory diagram showing a basic configuration of another example of the present invention.

FIG. 5 is an explanatory diagram explaining the prior art.

Explanation of Reference Numerals

- | | |
|-------|--|
| 1 | Pre-treatment catalyst layer |
| 2 | NH_3 decomposition catalyst layer |
| 15 3 | Flow path having NH_3 oxidation component |
| 4 | Flow path not having NH_3 oxidation component |
| 5 | Preheater |
| 6 | Stripping tower |
| 7 | Carrier gas |
| 20 8 | Diluted air |
| 9 | Catalyst tower |
| 10 | Neutralization tank |
| 11 | Pump |
| 12 | Noble metal-base oxidation catalyst layer |
| 25 13 | Treated gas |
| 14 | Gas to be treated |

Best Mode for Carrying Out the Invention

FIG. 1 is an explanatory diagram showing an NH_3 -containing gas purifier as an example of the present invention. In FIG. 1, a pre-treatment catalyst layer 1 composed of a flow path of a catalyst layer having a function for oxidizing NH_3 to generate NO and another flow path of a catalyst layer not having the former function, and an NH_3 decomposition catalyst layer 2 having a denitration function and a function for oxidizing NH_3 to generate NO in combination are disposed along the direction of a gas flow in a catalyst tower 9.

In the structure as described above, a high concentration NH_3 -containing gas as a gas to be treated 14 flows into the pre-treatment catalyst layer 1, and a part of the gas passes through the catalyst layer having the function for oxidizing NH_3 to generate NO, whereby a part of the NH_3 is converted into NO, while the NH_3 in the gas passing through the catalyst layer not having the function for oxidizing NH_3 is not oxidized, and passes through the pre-treatment layer 2. In this manner, the gas in which a part of the NH_3 is oxidized to generate NO and the NH_3 concentration thereof becomes suitable for the treatment in the downstream NH_3 decomposition catalyst layer 2 flows into the NH_3 decomposition catalyst layer 2, wherein the resultant gas is treated by the synergistic action of the denitration reaction and the NH_3 oxidation reaction described above, so that both of the NH_3 and NO concentrations are reduced down to several ppm or less.

According to the present example, since the pre-treatment catalyst layer 1 is provided with the catalyst layer containing a noble metal component and having the NH_3 oxidizing function, and the catalyst layer not having the former function in combination as described above, the NH_3 concentration can be reduced down to a concentration suitable for the treatment in the downstream NH_3 decomposition catalyst layer 2 after decomposing partially the NH_3 in the gas to be treated, even if the condition varies within a certain extent. In other

words, since the pre-treatment catalyst layer 1 is combined with the NH_3 decomposition catalyst layer 2, no unnecessary NO is by-produced, and NH_3 may be efficiently decomposed and treated.

In addition, according to the present example, an NH_3 -containing gas of
5 a high concentration, which had been hardly treated in a conventional technology because of deterioration of the catalyst and production of NO_x , can be removed highly efficiently without by-producing the NO_x . Accordingly, amounts of air and water vapor required heretofore for diluting the NH_3 concentration down to that being treatable may be reduced remarkably, so that
10 the running cost can be reduced. Besides, there are an advantageous effect of preventing deterioration of a catalyst due to reaction heat based on abnormal heating and another advantageous effect of being hardly affected by variations in the operation condition.

In the present invention, the expression "pre-treatment catalyst layer
15 composed of the catalyst layer having the function for oxidizing NH_3 to generate NO_x and another catalyst layer not having the former function" means a catalyst layer made of a catalyst body (honeycomb catalyst) having a configuration constructed such that each flow path forms a single flow path communicating from the inlet to the outlet such as a honeycomb made of
20 ceramics, for example, cordierite and the like; and a corrugate honeycomb made from an inorganic fiber nonwoven fabric, a metal sheet and the like. A part of its flow path section is composed of the catalyst body containing an NH_3 oxidation active component made of zeolite, silica, titania, zirconia, alumina or the like supported with platinum (Pt), palladium (Pd), or rhodium (Rh), while a
25 part of another flow path section is composed of another catalyst body not containing the above-described NH_3 oxidation active component.

Any configured arrangement may be applied as to a flow path area of the catalyst layer containing the oxidation active component and another flow

path area of the catalyst layer not containing the oxidation active component. For instance, a flow path area on which a catalyst component is supported in a configuration such as a striped pattern, a staggered pattern, a sea-island pattern and the like as shown in FIGS. 2(A), 2(B), and 2(C) is preferably used.

5 In case of forming the flow path of the catalyst layer containing a noble metal catalyst component and another flow path of the catalyst layer not containing the noble metal catalyst component, when the number of divided regions is increased, NH_3 oxidation reaction heat may be escaped from the flow path containing the noble metal catalyst to the flow path not containing the noble
10 metal catalyst. Thus, it may further prevent deterioration of the catalyst due to an abnormal temperature rise in an inlet part of the catalyst.

In the present invention, although there is no limitation as to a support amount of a noble metal as an oxidation active component in the pre-treatment catalyst layer, a preferable result can be obtained within the range of from 0.05
15 wt% to 10 wt% with respect to a carrier such as zeolite, and silica. On the other hand, a larger support amount of the noble metal as to an exhaust gas flow path is desirable, but increase in the support amount of such noble metal results in the price increase, and hence, the support amount is, for example, 0.01 g/liter or more, and preferably 0.1 g to 2 g/liter of the flow path.

20 In the present invention, the NH_3 decomposition catalyst having the denitration function and the function for oxidizing NH_3 to generate NO_x in combination may be, for example, a catalyst prepared by introducing thinly zeolite or porous silica on which Pt has been supported as a noble metal component into a mixture containing a titanium (Ti) oxide as the major
25 component and a vanadium (V) oxide as an active component for the denitration catalyst component, which is disclosed in Japanese Patent Application Laid-Open Nos. 5-146634 and 2000-317272. More specifically, the catalyst may be the one composed of a composition consisting of oxides of at

least one or more elements selected from titanium, vanadium, tungsten and molybdenum as a first component, and another composition being either salts of a noble metal selected from platinum, palladium, and rhodium or a material containing any of the above-described noble metals which has been previously
5 supported on a porous material such as zeolite, alumina, and silica as a second component. A configured arrangement of the NH_3 decomposition catalyst may be the same as that of the pre-treatment catalyst, for example, in which a variety of honeycomb-shaped carrier is supported with a catalyst component in accordance with a publicly known method. In this respect, however, the
10 invention is not particularly limited to that described above, but any configured arrangement such as a stacked layer body of plate-like catalyst is applicable.

In the present invention, a control for a supply amount of the NH_3 -containing gas to the flow path of the catalyst layer having the function for oxidizing NH_3 to generate NO and another flow path of the catalyst layer not
15 having the former function in the pre-treatment catalyst layer is carried out in accordance with a manner in which a ratio of existence of both the catalyst layers in their flow path parts is adjusted such that the NH_3 concentration in the outlet gas of the pre-treatment catalyst layer is higher than the NO_x concentration. In this case, when a ratio of NH_3 corresponding to an amount of
20 NH_3 which has been intended to be previously oxidation-decomposed in the pre-treatment catalyst layer is selected to become equal to a ratio occupied by the flow path of the catalyst layer having oxidation activity with respect to the whole gas flow path, the desired result is easily obtained.

FIG. 4 is a schematic diagram illustrating an example in which the
25 present invention is applied to a treatment of waste water discharged from a semiconductor plant and the like. In FIG. 4, the system is principally composed of a neutralization tank 10 for NH_3 -containing waste water, a preheater 5 and a stripping tower 6 connected to the neutralization tank 10 through a pump 11, a

catalyst tower 9 disposed on the downstream side of the stripping tower 6, and a pre-treatment catalyst layer 1 and an NH_3 decomposition catalyst layer 2 which are disposed sequentially along the direction of the gas flow in the catalyst tower 9. Reference numeral 7 designates a carrier gas, and reference numeral 8 designates a diluent air.

In the constitution as described above, the NH_3 -containing waste water first flows into the neutralization tank 10 in which the pH thereof is adjusted to be 7 or more by means of, for example, sodium hydroxide, then passes through the pump 11 and the preheater 5, and flows into the stripping tower 6 at a predetermined temperature. Thereafter, the ammonia is stripped to transfer to vapor phase. The gas containing the ammonia after stripping is diluted with air as necessary, and then, introduced into the catalyst tower 9 on the downstream side in which a part of NH_3 is converted into NO_x in the pre-treatment catalyst layer 1, whereby the resultant gas having an NH_3 concentration suitable for the treatment in the NH_3 decomposition catalyst layer 2 is obtained. Then, the gas flows into the NH_3 decomposition catalyst 2 in which NH_3 is decomposed efficiently into N_2 and H_2O by means of a balance of the denitration function and the function for oxidizing NH_3 to generate NO , and as a result, the gas is made to be harmless.

According to the present example, even if the waste water contains NH_3 of a high concentration, the NH_3 in the waste water may be transferred to a vapor phase, and then, made to be efficiently harmless. Furthermore, since a quantity consumed of diluent air and the like may be suppressed to the utmost in addition to downsizing of the system, whereby energy-saving of the whole system can be achieved.

In the following, specific examples of the present invention will be described.

Example 1

With respect to 50 g of hydrogen-substituted type Mordenite powder (HSZ-650, $\text{SiO}_2/\text{Al}_2\text{O}_3=23$ manufactured by Tosoh Corporation), a prescribed amount of an aqueous solution of chloroplatinic acid ($\text{HPtCl}_6 \cdot 6\text{H}_2\text{O}$) was added such that Pt was 0.5% in a weight ratio, the mixture was evaporated and dried, and then, the resulting product was calcined at 550°C for 2 hours to obtain a Pt-Mordenite catalyst. The resulting catalyst was slurried with silica gel and water, a commercially available corrugated honeycomb support made of a silica-alumina fiber (Honeycle 3722 having 150 square and 20 length manufactured by NICHIAS Corporation) was coated with the resultant slurry, and then, a honeycomb-structured Pt Mordenite catalyst was obtained after applying air-drying for 2 hours, drying at 120°C for 2 hours, and calcining at 500°C for 2 hours. A Pt support amount of the present catalyst was 0.75 g/L. The catalyst was cut off in 25 mm width to obtain a catalyst flow path part of $25 \times 150\text{-}20$ L containing an NH_3 oxidation component. It is to be noted herein that an omitted unit in case of expressing a size of a catalyst is always "millimeter" in the specification, and the same is applied to the following respective examples.

On the other hand, the same corrugated honeycomb support on which no catalyst component had been supported was cut off into a belt shape of $25 \times 150\text{-}20$ L, whereby a catalyst flow path part containing no NH_3 oxidation component was obtained.

The above-described flow path part containing the oxidation component was alternately stacked with the flow path part not containing the oxidation component in six plies, and then, the outer periphery of the stacked parts was surrounded by a metallic frame to obtain a catalyst material for the pre-treatment of 150 square-20 L (corresponding to the catalyst material shown in FIG. 2(A)).

On one hand, an oxidation catalyst layer to be disposed on the downstream side of an exhaust gas treatment was manufactured as follows. To 1 liter of 1.33×10^{-2} wt% of chloroplatinic acid ($\text{H}_2[\text{PtCl}_6] \cdot 6\text{H}_2\text{O}$) aqueous solution, 100 g of a fine silica powder (Micon F manufactured by Tomita Pharmaceutical Co., Ltd.) was added, the mixture was evaporated and dried on a sand bath, and the resultant product was calcined at 500°C in air for 2 hours to prepare 0.05 wt% Pt-SiO₂, thereby obtaining a catalyst powder of a first component. Aside from this, 7.43 kg of ammonium paratungstate ($(\text{NH}_4)_{10}\text{H}_{10}\text{W}_{12}\text{O}_{46} \cdot 6\text{H}_2\text{O}$) and 3.0 kg of ammonium metavanadate were added to 46.7 kg of a titanium oxide powder (MCH manufactured by Ishihara Sangyo Kabushiki Kaisha Ltd.; SO₄ content: 3 wt%), the resultant mixture was kneaded by the use of a kneader, the resulting paste was granulated and then, dried, thereafter calcined at 550°C for 2 hours. The resulting granules were pulverized to obtain a catalyst powder (Ti/W/V = 91/5/4 (atomic ratio) of a second component. A corrugated honeycomb support made of an alumina-silica fiber (Honeycycle 3722 having 150 square-100L manufactured by NICHIAS Corporation) was immersed into slurry obtained by suspending 2.0 kg of the resulting second component and 202 g of the first component into 306 kg of water, whereby the support was impregnated with the slurry. Thereafter, a liquid was drained off from the support by means of air blow, dried in atmosphere, and then, calcined at 500°C for 2 hours to obtain an NH₃ decomposition catalyst layer to be disposed in the exhaust gas downstream part.

Example 2

A pre-treatment catalyst layer was obtained in accordance with the same manner as that of the above described example 1 except that the preparing

method for the catalyst layer for the pre-treatment of example 1 was changed as described hereinafter.

The same corrugated honeycomb material made of the silica-alumina fiber (150 square-20L) used in example 1 was impregnated with 30% TiO_2 sol (manufactured by Ishihara Sangyo Kabushiki Kaisha Ltd.), thereafter a liquid was drained off by means of air blow, and dried at 150°C . The resulting material was cut off into pieces each having 30 breadth, thereafter three pieces were impregnated with a dinitrodiamineplatinum solution (Pt concentration: 1.33 g/L), dried again, and these pieces were calcined at 600°C together with the remaining two pieces. Both types of the resulting materials are alternately laminated with each other to obtain the catalyst layer for the pre-treatment.

Example 3

A pre-treatment catalyst layer was obtained in accordance with the same manner as that of the above described example 1 except that the preparing method for the catalyst layer for the pre-treatment of example 1 was changed as described hereinafter.

A commercially available honeycomb support made of cordierite (manufactured by Hitachi Metals, Ltd.; cell number 300 cpsi, 150 square-20L) was impregnated with alumina sol (manufactured by Nissan Chemical Industries, Ltd.; Al_2O_3 content 20%), a liquid was drained off from the resultant material, dried, and calcined at 450°C for 2 hours to obtain a support on which 30 g/L of Al_2O_3 was supported. A nitric acid solution of palladium nitrate (Pd concentration: 1 g/L) was poured into each single cell of the honeycomb material by the use of a dropper to prepare the support in which regions on each of which is supported with Pd and regions on each of which is not supported with Pd were made to be present in a staggered configuration as shown in FIG. 2(B). The resultant material was dried, and calcined at 600°C for

2 hours to obtain the catalyst layer for the pre-treatment. A Pd support amount in the Pd support regions in the present catalyst was about 2 g/L.

Example 4

5 A pre-treatment catalyst layer was obtained in accordance with the same manner as that of the above described example 2 except that the dinitrodiamineplatinum solution used in the preparation method of the catalyst layer for the pre-treatment in example 2 was replaced by a rhodium nitrate (Rh concentration: 0.65 g/L) solution. A Rh support amount in the Rh support
10 regions in the present catalyst was about 1 g/L.

[Comparative examples 1 to 4]

Catalyst layers of comparative examples 1 to 4 were prepared in accordance with the same manner as that of the above-described respective
15 examples except that the pre-treatment catalyst layers in the examples 1 to 4 were replaced by noble metal support catalysts of each 150 square-20L size which was prepared by such a manner that each material was supported entirely with each of the noble metal components in the pre-treatment catalysts.

Each of the pre-treatment catalyst materials obtained in the examples 1
20 to 4 and the comparative examples 1 to 4 was disposed along the gas flowing direction of a reactor on the upstream side, while the flow path on the downstream side was filled with the NH_3 decomposition catalyst prepared in the example 1, a gas (NH_3 : 3%, water vapor: 12%, the remainder: air) heated to 200°C or 300°C was supplied at 50 m^3/h from the inlet of the reactor on the
25 pre-treatment catalyst side, and concentrations of the remaining NH_3 and NO were measured in the outlet of the reactor. Reactor inlet temperatures, reactor outlet NH_3 concentrations and NO concentrations measured were shown in table 1.

[Table 1]

Treatment Manner	Reactor Inlet Outlet (°C)	Concentration in Reactor Temperature (ppm)	
		NH ₃	NO
Example 1	200	2	0.1
Example 2	200	4	0.1
Example 3	300	5	5
Example 4	300	3	4
Comp. Ex. 1	200	1 or less	8000
Comp. Ex. 2	200	1 or less	12000
Comp. Ex. 3	300	1 or less	9000
Comp. Ex. 4	300	1 or less	14000

As is apparent from table 1, scarce NH₃ was detected in the outlet of the reactor in any of the comparative examples 1 to 4, and production of a large quantity of NO was observed. On the contrary, both the concentrations of NH₃ and NO were treated so as to be 5 ppm or less in the examples 1 to 4. Accordingly, it has been found that the NH₃ can be decomposed and processed efficiently without by-producing a large quantity of NO_x in accordance with the present invention in which the pre-treatment catalyst is used.

Industrial applicability

There is a tendency to tighten regulations as to NH₃ in exhaust gases and waste water, so that it is considered that there will be more and more needs for an NH₃ decomposition technology. In these circumstances, the present invention can expand remarkably an NH₃ concentration range which may be treated with the multi-functional catalyst (NH₃ decomposition catalyst),

so that the invention may practice on an NH_3 -containing gas of a high concentration to which an application of a conventional multi-functional catalyst has been considered to be impossible, or required to apply such pre-treatment that the high concentration had been beforehand reduced by the use of a large
5 quantity of diluent gas; as a result of only an addition of a small amount of the pre-treatment catalyst. Therefore, the present invention can serve the above-described needs, and hence, the invention provides a technology with future potential.